Density discontinuities in short polymer chains modelled as hard-sphere sequences

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Abstract. Monte Carlo simulations of polymer chains containing up to fifteen hard-sphere repeat units have been carried out, the principal interest being the density distribution of the spheres in the neighbourhood of a rigid boundary. The density discontinuity recently reported by Croxton, in the direction normal to the boundary and at a distance of one sphere diameter from it, is confirmed, although there are considerable differences in the calculated densities very close to the boundary. It is shown that the amplitude of the discontinuity is largely independent of the self-avoiding (excluded volume) condition imposed on the growing chain, but is approximately halved when the rigid boundary restraint is removed. The discontinuity originates mainly in the distribution of the second sphere of the chain sequence. The details of the configurational features of the chains are largely in agreement with Croxton's findings, although trains consisting of more than two spheres have been found. The exponent γ in the expression $\langle R_N^2 \rangle \propto (N-1)^\gamma$, where $\langle R_N^2 \rangle$ is the mean square end-to-end length of a chain containing N spheres, is evaluated at ~ 1.37 for $3 \leq N \leq 15$.

1. Introduction

In a recent series of papers, Croxton (1983, 1984, 1985, 1986, 1987) has investigated the configurational properties of perfectly flexible short self-avoiding polymer chains in the vicinity of a rigid planar boundary. He developed convolution (c) and iterative convolution (ic) estimates (Croxton 1983, 1984 respectively) of the normalized spatial probability density distribution function $Z(z_i, N)$ of the ith segment of a chain containing N segments or mers; the z-direction is normal to the planar boundary. He compared these estimates with the results of a Monte Carlo (mc) simulation (Croxton 1986) in which the individual segments of the chain were modelled as self-avoiding hard spheres, the centres of succesively added spheres being separated by a distance equal to the sphere diameter.

An interesting feature common to these three results was a marked discontinuity in the probability density distribution function

$$\rho(z, N) = \sum_{i=2}^{N} Z(z_i, N)$$

at a distance equal to one segment diameter from the boundary, the ic calculation also showing smaller discontinuities at distances of two and three segment diameters.

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Such discontinuities contrast sharply with the essentially structureless density distributions of Dickinson and Lal (1980), and with the small diffuse peaks at low multiples of the segment diameter obtained from a variety of analytic and simulation techniques (Percus 1976, Henderson *et al* 1976, Waisman *et al* 1976, Blum and Stell 1976, Snook and Henderson 1978, Henderson and Van Swol 1984, Dickman and Hall 1988).

We present here the results of an MC simulation, essentially a repetition of Croxton's work, which confirms the existence of a discontinuity in $\rho(z, N)$ at $z = 1$. However, our $\rho(z, N)$ is in much better agreement with the IC prediction in the small-z region, and the details of the tails/loops/trains structure of the chains close to the boundary differ significantly from those given by Croxton. We show also that while the amplitude of the discontinuity is slightly reduced by the excluded volume condition, it is almost doubled by the rigid planar boundary constraint; the discontinuity originates essentially in the angular distribution of the centre of the second sphere of the chain at a fixed distance from the first.

2. The Monte Carlo chain generation process

The chain generation process adopted here is very similar to that described by Croxton (1986). The Nth repeat unit (mer) of the polymer chain is represented by a sphere of unit diameter whose centre is separated from those of the $(N - 1)$th and $(N + 1)$th spheres by unit distance. The centre of the first sphere is located at $(0, 0, 0)$, and the presence of the rigid planar boundary at $z = -0.5$ requires that the centres of all other spheres have z-coordinates $\geqslant 0$. The excluded volume condition is violated if the centre of the next sphere which it is proposed to add to an existing sequence is within less than unit distance of any other centre, and in that case the chain is discarded, although the configurational statistics up to and including the last acceptable sphere are of course added to the running totals being compiled for averaging.

Croxton (1986) emphasizes the importance of choosing the location of the centre of the $(N + 1)$th sphere at random on the spherical surface of unit radius centred on the Nth sphere. To do this he adopts a procedure described by Knuth (1969), in which independent x, y, z coordinates normally distributed over the interval $(-1, 1)$ are generated, and the coordinates of the $(N + 1)$th centre relative to the Nth are then taken as $x' = x/r$, $y' = y/r$ and $z' = z/r$ where $r = (x^2 + y^2 + z^2)^{1/2}$. Here we have adopted a simpler and certainly faster procedure (Smith and Fleming 1975) in which $\cos\theta$ (where θ is the bond angle) is uniformly distributed over the interval $(-1, 1)$, and the azimuthal angle ϕ is uniformly distributed $(0, 2\pi)$. A check of this procedure combined with the random number generator routine was made by generating 10^6 points (x, y, z) and inspecting the separate x, y and z distributions within 0.025-wide intervals; the departure from an ideally random distribution (25 000 samples in each interval) was less than 2%.

3. Results and discussion

3.1. Segment density distributions

In figure 1 we compare the density distribution $\rho(z, 15)$ for a 15-mer chain constrained by a rigid boundary at $z = 0$ with the corresponding distributions obtained by Croxton from his MC and IC calculations. The present results were obtained by averaging over 300 000 15-mer chains, about 30% of the corresponding number of chains in Croxton's
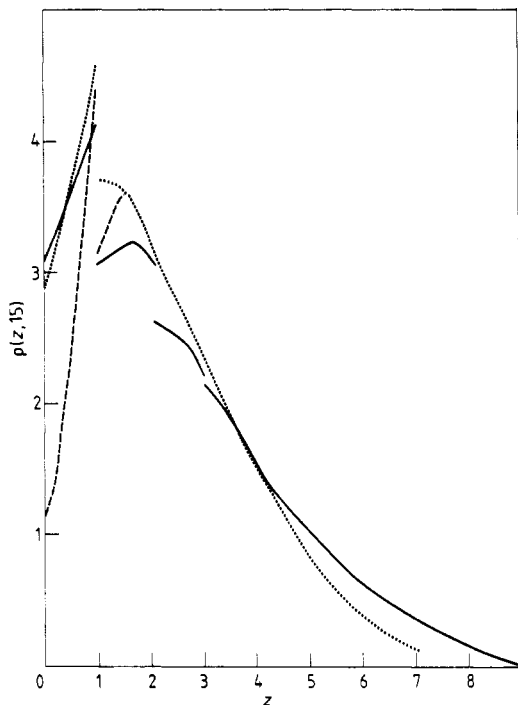
Figure 1. Total segment density distribution $\rho(z, 15)$ against z. Full curve: Croxton, iterative convolution analysis. Broken curve: Croxton, Monte Carlo simulation. Dotted curve: present Monte Carlo simulation, 300 000 15-sphere chains.

sample. The horizontal axis scale is in multiples of the sphere diameter. The discontinuity in $\rho(z, 15)$ at $z = 1$ is clearly seen in each distribution, although its amplitude varies from around 0.9 in the present work to about 1.25 in Croxton's MC data. The smaller discontinuities at $z = 2$ and $z = 3$ predicted by IC are both missing from both MC results, although the number of MC samples might not be sufficiently large to resolve the $z = 3$ case. There is little difference between the two MC results for $z > 1.5$; however, in the region $0 < z < 0.9$ the present MC data are in better overall agreement with the IC result, while for $1 < z < 1.5$ the sharply increasing density in Croxton's MC data better reflects the IC pattern. These differences are surprising, given that the two sets of MC data differed by not more than 0.6%, 0.3% and 0.15% in respect of $\langle R_N^2 \rangle$, $\langle z_N^2 \rangle$ and $\langle z_N \rangle$ up to $n = 15$; $\langle R_N^2 \rangle$ is the mean square end-to-end length of a chain consisting of N spheres, and the other two quantities are defined analogously. Furthermore, the attrition rate, i.e. the decrease in the number of samples with increasing chain length, due to the excluded volume constraints, was almost identical. More specifically, the ratio (number of 15-sphere chains)/(number of 2-sphere chains) was 0.003 141 in the present work and 0.003 148 in Croxton's.

As a partial check of the present programme we set the excluded volume to zero and re-ran the simulation with the rigid boundary constraint removed, the centre of the first sphere still being fixed at $(0, 0, 0)$. Averaging over 10^6 15-sphere chains we obtained the expected result $\langle R_N^2 \rangle = N - 1$ (Flory 1953) for $2 \leqslant N \leqslant 15$. The corresponding $\rho(z, 15)$ density distribution for the $z > 0$ region is shown in figure 2, and comparing with figure 1 we see that, as expected, removal of the excluded volume and rigid
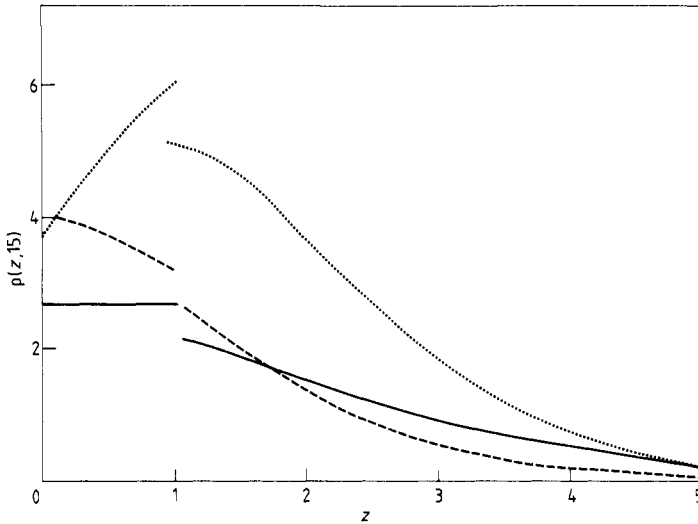
Figure 2. Total segment density distribution $\rho(z, 15)$ against z. Full curve: normal excluded volume, no boundary, $z > 0$, 300 000 15-sphere chains. Broken curve: zero excluded volume, no boundary, $z > 0$, 10^6 15-sphere chains. Dotted curve: zero excluded volume, rigid boundary at $z = 0$, 10^6 15-sphere chains.

boundary constraints results in larger densities close to $z = 0$. The sharp increase in density which occurs between $z = 0$ and $z = 1$ in the presence of the rigid boundary becomes a slower decrease in its absence; in both cases a well defined discontinuity occurs at $z = 1$, its amplitude being nearly doubled in the presence of the boundary. An almost identical result was obtained for the $z < 0$ region.

We show also in figure 2 the $\rho(z, 15)$ distributions for (i) normal excluded volume (sphere diameter $= 1$) in the absence of a rigid boundary, $z > 0$ region, and (ii) zero excluded volume in the presence of a rigid boundary. In both cases a discontinuity occurs at $z = 1$. Inspection of the detailed computer printouts shows that removal of the excluded volume constraint slightly increases the amplitude of the discontinuity, e.g. from 0.93 to 0.96 in the presence of the boundary and from 0.52 to 0.58 in its absence. On the other hand, for constant excluded volume, introduction of the boundary almost doubles the amplitude. In all cases the amplitude is very close to that generated exclusively by the 'sharp' edge of the density distribution of the centre of the second sphere of the sequence. This density is constant at 1.0 and 0.5 over the z-ranges $(0, 1)$ and $(-1, 1)$ respectively, corresponding to presence or absence of the barrier, and falls to zero at $z = \pm 1$. The distributions of subsequent spheres influences the discontinuity only slightly. Particularly noteworthy is the constant $\rho(z, 15)$ in the z-range $(-1, 1)$ for the case of normal excluded volume and no boundary, where for all $N > 2$ the density is constant within this range and then decreases, the rate of decrease becoming slower for higher N.

We investigated the influence of the second sphere further by synthesizing chains in which the locus of the $(N + 1)$th sphere was not randomly distributed over the surface of a sphere of unit radius centred on the Nth sphere. Specifically we generated three independent random numbers x, y, z uniformly distributed in the range $(-1, 1)$, and then took the coordinates of the centre of the $(N + 1)$th sphere relative to the centre of the Nth as x/r, y/r, z/r where $r = (x^2 + y^2 + z^2)^{1/2}$. In the case of zero

excluded volume and a rigid boundary the density distribution of the second sphere peaks around $z = 0.7$, falling from 0.57 at $z = 0.7$ to zero at $z = 1$ This is mirrored in the $\rho(z, 15)$ distribution shown in figure 3, where the amplitude of the discontinuity at $z = 1$ is 0.55.
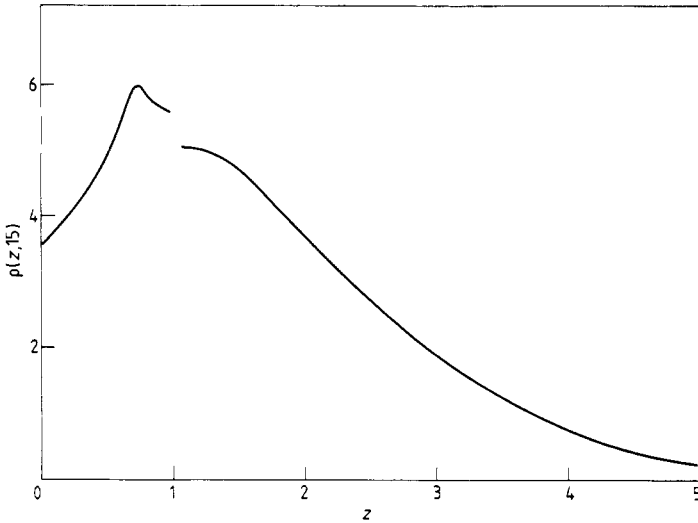

Figure 3. Total segment density distribution $\rho(z, 15)$ for 10^6 15-sphere chains, zero excluded volume, rigid boundary at $z = 0$. The centre of sphere N relative to that of sphere $N - 1$ was determined by generating x, y and z independently and uniformly in the range $(-1, 1)$ and normalizing according to $(x^2 + y^2 + z^2)^{1/2} = 1$.

3.2. Loops, tails and trains

Adopting the physical definitions of loops, tails and trains given by Croxton (1986), we calculated the mean length of each formation, i.e the mean number of spheres they contain, as a function of the total number of spheres in the chain. The contact parameter ζ was 0.0625, a sphere the ζ-coordinate of whose centre is less than ζ being considered adsorbed at the boundary. The definitions of the lengths of loops, tails and trains adopted in the present work are as follows.

(a) Loops. If the spheres numbered p and q along a given chain are adsorbed, and all the spheres between them are desorbed, then the loop so formed has length $q - p - 1 \; (q > p + 1)$.

(b) Tails. If the chain contains a total of N spheres, and sphere q is adsorbed, and no other sphere between q and N is adsorbed, then the tail so formed has length $N - q$.

(c) Trains. A train has length $p \; (\geq 1)$ if it consists of p consecutively adsorbed spheres, with the proviso that the first sphere of any chain (fixed at the origin) is not included in any train.

As shown in figure 4, the tails in the present simulation are on average about one sphere longer than those in Croxton's work, while the loops are about 0.5 spheres shorter. Croxton does not specifically define the lengths of tails and loops, but it is
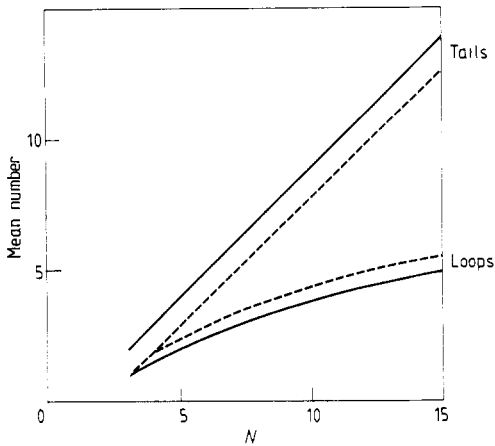
Figure 4. Mean number of spheres in tails and loops against the total number N of spheres in the chain, for chains subject to excluded volume constraints and with a rigid boundary at $z = 0$. The contact parameter ζ is 0.0625. Full curve: present Monte Carlo simulation. Broken curve: Croxton Monte Carlo simulation.

unlikely that both these discrepancies arise entirely from different definitions. Nevertheless, the marked dominance of tails containing all but the first sphere, independent of chain length, is confirmed, as also is the tendency to form very long or very short loops in preference to those of intermediate length, for a given chain length (see table 1 for 15-sphere chains).

The average length of trains in the present work is around 1.034, varying very little with chain length. Thus nearly all adsorbed spheres are adsorbed in isolation, very few trains containing two or more spheres, as shown in table 1 for 15-sphere chains. However, there are *some* such trains, contrasting with Croxton's finding that trains *never* exceed two spheres in length.

Table 1. Sizes and numbers of loops, trains and tails for $N = 15$. The size column gives the number of spheres incorporated in each configurational feature. 300 000 15-sphere chains were generated with excluded volume and rigid boundary restraints applied. The contact parameter was 0.0625.

Size	Loops	Trains	Tails
1	3 164	20 713	400
2	1 462	684	369
3	984	17	273
4	689	0	314
5	503	0	330
6	436	1	399
7	400	0	422
8	333	0	517
9	319	0	678
10	283	0	973
11	385	0	1 465
12	418	0	3 071
13	1 024	0	10 399
14	0	0	279 213

We show in figure 5(a) the loop, tail and train component fractions, i.e. the percentages of the spheres incorporated in these configurational features, as functions of the number of spheres per chain; the corresponding data obtained by Croxton are shown for comparison in figure 5(b). There is good agreement on the order of magnitude of the various percentages, and the higher percentage of spheres incorporated in short trains found in the present work is consistent with our higher $\rho(z, 15)$ at low z. When the contact zone thickness ζ was reduced from 0.0625 to 0.007 28 the component fraction of tails exceeded 99% for $N \geqslant 3$, in agreement with Croxton, but the loops/trains cross over around $N = 6$ persisted. The dominance of tails over loops and trains arises from the absence of an attractive sphere-boundary attraction, and hence a rapidly decreasing probability that the chain will return to the boundary as its length increases.

3.3. Mean square end-to-end length

The plot of $\log_{10}\langle R_N^2\rangle$ against $\log_{10}(N - 1)$ shown in figure 6 suggests the relationship $\langle R_N^2\rangle \propto (N - 1)^{1.37}$. Croxton followed a procedure due to Whittington (1975) and plotted γ_n against $1/n$, where $\gamma_n = (n/2)((\langle R_{N+1}^2\rangle/\langle R_{N-1}^2\rangle) - 1)$ as $n = N - 1$; he deduced a limiting value $\gamma_\infty \sim 1.20$, although there is considerable scatter in the γ_n against $1/n$ plot, and so the accuracy of the extrapolation to $1/n = 0$ is doubtful. Nevertheless the result $\gamma_n \sim 1.20$ is consistent with the findings of Whittington (1975) and Guttmann *et al* (1978), who used exact enumeration techniques on a variety of lattices. On the other hand $\gamma_n = 1.37$ (figure 6) is in good agreement with the exact enumeration studies of Mark and Windwer (1974) for the case of zero adsorption energy. It may be of course that γ_n decreases with increasing n, but such a decrease would appear to be very slow.
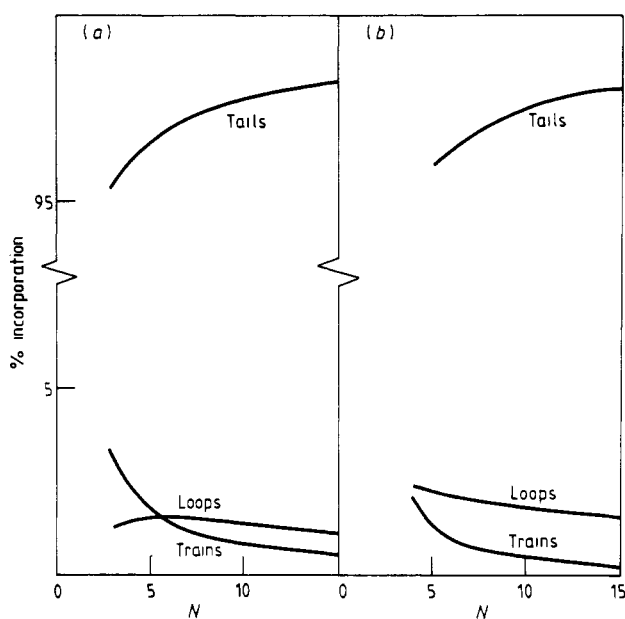

Figure 5. Percentages of spheres incorporated in tails, loops and trains against the total number N of spheres in the chain, for chains subject to excluded volume constraints and with a rigid boundary at $z = 0$. The contract parameter ζ is 0.0625. (a) Present Monte Carlo simulation. (b) Croxton Monte Carlo simulation.
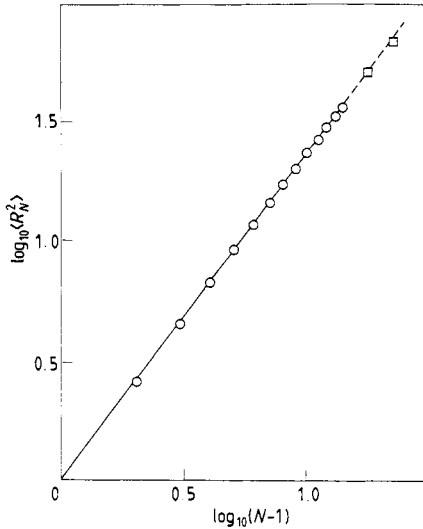
Figure 6. $\mathrm{Log}_{10}\langle R_N^2\rangle$ against $\log_{10}(N-1)$, where $\langle R_N^2\rangle$ is the mean square end-to-end length of a chain containing N spheres. The slope is ~ 1.37. The two uppermost points ($N = 19$, 24) are taken from Croxton (1986), figure 3. We quote $\langle R_{15}^2\rangle = 37.000 \pm 0.034$, $\langle R_8^2\rangle = 14.602 \pm 0.003$ to illustrate typical standard errors in the $\langle R_N^2\rangle$ values.

Plots of $\log_{10}\langle z_N^2\rangle$ and $\log_{10}\langle z_N\rangle$ against $\log_{10}(N-1)$ have slopes of 1.42 and 0.71 respectively. $\langle R_N^2\rangle$ is always at least twice $\langle z_N^2\rangle$, suggesting lateral spreading of the chain in preference to growth normal to the boundary.

4. Conclusions

The main conclusions to be drawn from the present work are as follows.

(i) The existence of a discontinuity in the segment density distribution of a short polymer chain terminally attached to a rigid boundary, at a distance equal to one segment diameter from the boundary, has been confirmed by Monte Carlo simulation.

(ii) The amplitude of this discontinuity is slightly reduced if the self-avoiding condition imposed on the growing chain is removed, but is approximately halved when the chain is not constrained by the boundary. It originates almost entirely in the density distribution of the second sphere of the sequence.

(iii) The preponderance of tails over loops and trains is also confirmed, although the formation of trains exceeding two spheres in length has been observed, contrary to the findings of Croxton. This discrepancy may originate in the higher segment densities close to the rigid boundary found in the present simulations.

Acknowledgments

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